# PRODUCTION OF PLASTIC FROM MARINE ALGAE

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## ABSTRACT

The two objectives of this research are to produce plastic that is environmental friendly whereby the plastic produced can be at least slightly decomposed to smaller substances by the living organisms from marine algae and also to characterize the plastic that have been produced from the marine algae via mechanical and physical testing. In this study, algae which are Red *Eucheuma cottonii* are the raw material whereby Low Density Poly Ethylene (LDPE) is the additional plasticizer which aids in the plastic production. Chemical pretreatment was carried out on samples. The samples were then extruded by using twin screw extruder at temperature of 150 ºC and 50 RPM. The extruded samples are then inject molded and characterize by using Fourier Transform Infrared Spectroscopy (FTIR), melt flow index (MFI), tensile testing and density test. From the results obtained, it was found out that this species of algae is not suitable to be the raw material due to the weak properties of intermediate product which is the product after the extrusion process. During the experiments, those algae were difficult to extrude due to easier moisture absorbance from the environment that lead to failure in injection molding during the sample preparation. Hence it can be concluded that the formulation using this species are not suitable for injection molding purpose.

## ABSTRAK

Terdapat dua objektif utama dalam kajian ini iaitu untuk memproses plastic yang tidak mencemarkan alam sekitar di mana plastik tersebut mempunyai kebolehan untuk biodegradasi oleh kehidupan organisma di samping menyifatkan plastik yang telah dihasilkan melalui kajian mekanikal dan fizik. Red Eucheuma cottonii merupakan bahan mentah untuk kajian ini manakala LDPE merupakan bahan tambahan yang membantu dalam penghasilan plastik. Rawatan kimia telah dijalankan atas sampel. Sampel tersebut disediakan untuk proses pengusiran pada suhu 150 ºC dan 50 RPM. Sampel kemudian dibentukkan melalui suntikan dan disifatkan melalui FTIR,MFI ,ujian untuk menguiji kekuatan plastic yang telah dihasilkan dan juga ujian ketumpatan.. Hasil kajian didapati spesies ini tidak sesuai untuk kajian ini.disebabkan penyerapan wap air dari sekeliling yang menyebabkan susah untuk proses pengusiran. Dengan ini boleh disimpulkan bahawa composisi yang digunakan bagi spesies ini tidak sesuai untuk proses suntikan yang akan menghasilkan bentuk yang khas.

# TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| Gly | : Glycine |
| Ala | : Alanine |
| Thr | : Thyrosine |
| Met | : Methionine |
| RPM | : Rotations Per Minute |
| LDPE | : Low Density Poly-Ethylene |
| HDPE | : High Density Poly-Ethylene |
| FTIR | : Fourier Transform Infrared Spectroscopy |
| MFI | : Melt Flow Index |
| SDDS | : Sodium Dodecyl Sulfate |
| EL | : Elongation at Break |

# LIST OF SYMBOLS

lf: Distance between the marks at or as close as possible to failure

lo: Distance between the marks inked on the specimen before stretching

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of the Study

Marine algae are a type of phytoplankton (plant life), seaweeds in corals or anemones that is flower without petals. There are three common groups of marine algae that are green algae, brown algae and red algae. Sources of marine algae depend on the climate. For instance, green algae are largely aquatic or marine which can be found on the trunks of the trees, while brown algae can be found in colder oceans of the world and red algae commonly grown in warm-temperature and tropical climates. Marine algae is used in the production of plastic due to its advantage as a biodegradable plastic where it can be decomposed into smaller substance by living organisms. Basically biodegradability is defined as a process where all material fragments is consumed by microorganisms as a food and energy source. In this case, majority of the plastics fall into the category of petro-plastics and this petroleum based plastics are considered to be non-biodegradable or at best only biodegrade slowly which would end up as litter or in landfills. Therefore, algae based plastics is considered to be environmental- friendly as a biodegradable plastic. This is because marine algae undergoes photosynthesis process like other plants to harness sunlight and carbon dioxide and the energy produced is stored in the cell as lipids and form of carbohydrates. On the basis of these findings, it can be inferred that plastic produced from marine algae can solve two major problems that are air pollution resulting from carbon dioxide evolution and the second one is that solving future crises due to a shortage of energy resources which eventually make them an important innovation of sustainable development. Marine algae are being used due to its unique characteristics that can contribute to the production of plastic. Marine algae also have been reported to contain more unusual substances, such as low molecular-weight sulfides and amines as well as industrial precursor molecules, such as acrylic acid used in the production of plastics. Besides that, for several years there were studies in producing plastics from vegetable materials such as corn and other starches. However, these largely starch-based materials are often not well suited for many applications of solid packing foams because of their relatively rapid breakdown under wet conditions, and their inherently low breaking strengths. If we turn that food into plastic, it becomes more expensive-too expensive for the poor peoples in the third world ((WO/1994/017132) ALGAL PLASTICS). Moreover, algae can grow extremely fast in very large quantities at a very low price. When people talk about "seaweed" they are actually talking about one form of algae. Thus when talking about in the context of bioplastics, red algae also known as "red seaweed". Since there are many types of algae, only one specific type of algae is taken into consideration for the production of plastic. Red algae are chosen for this research due to high level of protein as compared to green and brown algae which is more feasible to produce plastic. This is because plastic is a polymer and red algae consists of protein chains that are also one type of natural polymer that can be processed to produce plastic. The organisms specified for use of this research are red algae of the species *Red Eucheuma Seaweed* of the Division (Rhodophyta) and Class (Rhodophyceae) ( Kathleen M.Cole et al.,1990). *Eucheuma* is a genus of tropical red seaweed that grows on limestone-rich substrates, especially coral reefs. Basically, the plastic is produced by breaking off the peptide links that connects the amino acids to form the protein by a process called protein denaturizing. This can be done by adding plasticizer and undergoes extrusion process together with some tensile tests for the strength of the plastic being produced. Thus, like all other plastics, bioplastics are composed of three basic parts which are one or more polymers, one or more plasticizers and finally plus one or more additives. Roughly speaking, polymers basically give plastic its strength; plasticizers give it its bendable and moldable qualities, and additives give the plastic produced other properties such as color, durability and so on.

## 1.2 Problem Statement

This research is being conducted in order to identify whether or not the species of algae used is ideal for the production of plastic.

Besides that, this research is to determine the optimum percentage composition of algae and additional plasticizer that gives the satisfactory strength of the plastic produced.

## 1.3 Objective

There are two main objectives in this research of producing plastic from marine algae.

The first objective is to produce plastic that is environmental friendly whereby the plastic produced can be at least slightly decomposed to smaller substances by the living organisms from marine algae.

The second objective is to characterize the plastic that have been produced from the marine algae via mechanical and physical testing.

## 1.4 Scope of Research

The scopes of study in this research are about the description and the characteristics of marine algae that help in the production of plastic. Moreover, the precise scope regarding the protein denaturizing of the marine algae by chemical treatment by using sodium dodecyl sulfate (SDS) and also conducting tests such as tensile tests in order to determine the strength of the plastics being produced from the marine algae.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

When the question arises the differences between bio plastics and biopolymers, this is how both of it are defined. As said in the portal of BioBasics (BioBasics, www.biotech.gc.ca), biopolymers were defined as polymers which are present in, or created by, living organisms. These include polymers from renewable resources that can be polymerized to create bio plastics. On the other hand, the portal also said that bio plastics are plastics manufactured using biopolymers, and are biodegradable. Today, bio plastics are gaining popularity once again as new manufacturing techniques developed through biotechnology are being applied to their production. Basically, there are two types of biopolymers which are those that come from living organisms; and, those which need to be polymerized but come from renewable resources. Both types are used in the production of bio plastics. Besides that from the website of Wikipedia , bio plastics or organic plastics are forms of plastics derived from renewable biomass sources such as vegetable oil, corn starch, and pea starch unlike fossil-fuel plastics derived from petroleum. Bio plastics provide the twin advantages of conservation of fossil resources and reduction in $CO_2$ emissions, which make them an important innovation of sustainable development. Algae serve as an excellent feedstock for plastic production owing to its many advantages such as high yield and the ability to grow in a range of environments. Algae bioplastics mainly evolved as a byproduct of algae bio fuel production, where companies were exploring alternative sources of revenues along with those from bio fuels. In addition, the use of algae opens up the possibility of utilizing carbon, neutralizing greenhouse gas emissions from factories or power plants. Algae based plastics have been a recent trend in the era of bio plastics compared to traditional methods of utilizing feedstock of corn and potatoes as plastics. While algae-based plastics are in their infancy, once they are into commercialization they are likely to find applications in a wide range of industries.

## 2.2 Classification of Seaweeds

Seaweeds can be classified into three broad groups based on pigmentation: brown, red and green reported from the thesis by Khaled (1999). From the website (marinelife.about.com), red algae have its often brilliant color due to the pigment phycoerythrin. These facts regarding red algae were obtained from (http://www.lenntech.com/eutrophication-water) noting that Rhodophyta, phylum of the kingdom protista consisting of the photosynthetic organisms commonly known as red algae. In most algae the primary pigment is *chlorophyll*, the same green pigment used in plants. Many algae also contain secondary pigments, including the *carotenoids*, which are brown or yellow, and the *phycobilins*, which are red or blue. Secondary pigments give algae their colorful hues. The red algae are multicellular and are characterized by a great deal of branching, but without differentiation into complex tissues. Most of the world's seaweeds belong to this group. Although red algae are found in all oceans, they are most common in warm-temperate and tropical climates, where they may occur at greater depths than any other photosynthetic organisms. Most of the coralline algae, which secrete calcium carbonate and play a major role in building reefs, belong here. Red algae are a traditional part of oriental cuisine. There are 4000 known marine species of red algae where a few species occur in fresh water. These algae can live at greater depths than brown and green algae because it absorbs blue light.

Besides that, red algae are most common in warm-temperature and tropical climates, where they may occur at greater depths than any other photosynthetic organisms. Red algae are chosen as the species to be used as the raw material for the production of plastics from marine algae. This is because red algae have the high amount of amino acids which act as the building blocks for the formation of protein which makes it also a natural polymer was found in the species belonged to Rhodophyta (red algae) as compared to Phaeophyta and Chlorophyta reported by Nirmal *et al*., 2010. Besides that an article from BioBasics said that there are also growing plants in plastic. In this era, plants have eventually become the factories for the production of plastics and this is proven by researches creating bacteria known as Arabidopis thaliana plant through genetic engineering. Basically, this plant contains specifically the enzymes which are used by the bacteria to create the plastic. Through the conversion of sunlight into energy the bacteria create the plastic. Moreover, the researches have transferred the gene that codes for this enzyme into the plant and via its cellular processes the plant produces plastic. The plant is then harvested and later the plastic is extracted from it using solvent. Separation involving between the solvent from the plastic are done in order to remove the liquids resulting from the process.

## 2.3 Proteins in Red Algae

### 2.3.1 Amino Acids in *Eucheuma cottonii*

There are many types of amino acids present in red algae and all the protein contents are used in this research field in order to achieve a substantial dimensional stability of the plastics produced similar to the synthetic plastics .The table below can be used as a tool to identify the types of protein that can contribute to the production of plastics from marine algae. Table 2.1 shows the amino acid concentration and total nitrogen content in *Eucheuma cottonii* reported by Patricia Matanjun *et al.* 2007.

**Table 2.1** Amino acid concentration and total nitrogen content in *Eucheuma cottonii*

| Amino Acids | (mg g−1 dry weight) |
|---|---|
| Aspartic acid (Asp) | 2.65±0.15 |
| Glutamic acid (Glu) | 5.17±0.13 |
| Serine (Ser) | 1.92±0.04 |
| Glycine (Gly) | 2.27±0.32 |
| Histidine (His) | 0.25±0.10 |
| Arginine (Arg) | 2.60±0.14 |
| Threonine (Thr) | 2.09±0.01 |
| Alanine (Ala) | 3.14±0.11 |
| Proline (Pro) | 2.02±0.09 |
| Thyrosine (Tyr) | 1.01±0.12 |
| Valine (Val) | 2.61±0.07 |
| Methionine (Met) | 0.83±0.17 |
| Isoleucine (Ile) | 2.41±0.04 |
| Leucine (Leu) | 3.37±0.06 |
| Phenylalanine (Phe) | 19.07±2.48 |
| Lysine (Lys) | 1.45±0.48 |
| Chemical score (%) | 25.6 |
| Most limiting amino acid | lysine |
| Total amount | 52.86±3.37 [c] |
| Essential amino acid (EAA) | 32.07±3.13 [b] |
| EAA (%) | 60.59±1.36 [a] |
| Protein (%) | 9.76±1.33 [a] |

Values are expressed as mean ± standard deviation, n=3

Values in the same row with different superscripts letters are significantly different ($p<0.05$)

Chemical score % = (mg limiting amino acid per g of test protein X 100)
(mg limiting amino acid per g of reference protein)

(No. based on FAO/WHO/UNU amino acid requirement pattern)

@ limiting amino acids

Based on the Table 2.1, I have found out that phenylalanine has the highest content in this species.

### 2.3.2 Experimental Absorption Frequencies of few Amino Acids using FTIR (Fourier Transform Infrared Spectroscopy)

As discussed by the researches such as Rolf *et al.,* 2007, they have identified the absorption frequencies for non aromatic amino acids. They have presented on the first gas phase Fourier Transform Infrared Spectroscopy (FTIR) spectra of the natural amino acids glycine, alanine, threonine, cysteine and methionine. It is revealed that matrix isolation spectroscopy has OH stretch, C=O stretch, $NH_2$ bend and COH bend vibration frequencies of glycine at 3560, 1790-1800, 1622-1630 and 1100 $cm^{-1}$ which was in good agreement with their research which show acceptable values which are 3577,1787,1620 and 1114 $cm^{-1}$. Based on the table 2.2, it shows the absorption frequencies of few selected amino acids such as glycine (Gly), alanine (Ala), threonine (Thr), cysteine (Cys) and methionine (Met). This would help in my research as I could identify the presence of amino acids by determining the functional groups.

**Table 2.2** Experimental absorption frequencies ($cm^{-1}$) of glycine (Gly), alanine (Ala), threonine (Thr), cysteine (Cys) and methionine (Met)

| Functional Groups | Gly | Ala | Thr | Cys | Met |
|---|---|---|---|---|---|
| OH ipb(COOH) | 1114 | 1114 | 1114 | 1118 | 1117 |
| CH/NH bend | 1620 | - | 1282<br>1377<br>-<br>-<br>1614 | -<br>1364<br>-<br>-<br>1627 | -<br>1369<br>1442<br>-<br>1630 |
| C=O | 1787 | -<br>1372<br>-<br>1590<br>1627 | 1779 | 1782 | 1777 |
| CH | 2937/2868<br>2951 | 1785 | -<br>2928<br>2981 | -<br>2952<br>- | 2860<br>2930<br>- |
| OH (COOH) | 3577 | -<br>2924<br>2991 | 3570 | 3572 | 3572 |
| OH | - | 3575 | 3652 | - | - |

### 2.3.3 Protein Denaturization and Denaturants

The researches Gonzalez *et al.*, 2009, found out that the in order for the formation of protein based bioplastics; there are three most essential steps for it to occur. The three steps are the stabilized intermolecular bonds are break off, mobile polymer chains are oriented in the desired shape and finally allowing the formation of new intermolecular bonds that strengthen the three –dimensional network. Besides that, denaturation of protein which is caused by heat results whereby in this case they used albumen. This is due to exposure of these sulfhydril groups which accompanied by a decrease in its total content due to oxidation to disulfide bonds reported by Van der Placken *et al.*, 2005.Thus according Gonzalez *et al.*, 2009 proteins chains unfold and entangle with other proteins, and new bonds arise, causing the texture to change.

In order to denature the proteins in the algae few researches such as Rakesh *et al*., 2002, certain reagents such as urea and sodium disulphide are added to denature protein as well as improve the gluing strength and their water resistance of the protein structure. However, in this journal they did research on soybean plastics that are protein based plastics. This research is almost similar to my undergraduate research since they are using the protein chains and I can use this as a reference to conduct my project. It was also discussed in this journal that the concentration urea had a significant effect on the extent of protein unfolding and ultimately on the adhesive properties (Plasticsnews.com/headlines).

## 2.4 Additives for Algal based Plastics

In my research I will be using LDPE (Low Density Poly Ethylene) as a form of additives to enhance the sample preparation as well as to improve the final product. From the book Additives can be categorized into 5 factors such as:

a) processing aids as to improve the process ability

b) antioxidants or stabilizers

c) mineral fillers as in to bulk out of the polymer

d) impact modifiers for example glass fibres to increase the strength

e) compatibilisers as in to improve mixing of two or more polymers (Polymers, The Environment and Sustainable Development)

LDPE has a better chance to act as impact modifiers or plasticizers at the same time in order to increase the strength of the algal plastics produced. These are the following characteristics of LDPE. LDPE is light and it has a good impact resistance besides having a good flexibility which would improvise the properties of the algal plastics to be produced. Most importantly, LDPE has a thermoforming performance that will assist in the extrusion process of the modified alginate that is added with the chemical composition. Moreover LDPE also has no moisture absorption since algae itself has a higher water content whereby the addition of LDPE is hoped to reduce the water content (Menasha Corporation).

## 2.5 Latest Discoveries

It is found out that a company called Cereplast has come with some invention to improvise the algal based bio plastics. Currently they have inject molded the algal based biomass together with polypropylene. Besides that, they have also tried with materials like corn, starch and tapioca in order to produce bio plastics. However, algae have a better demand in terms of producing bio plastics as compared to corn, starch and so on due to the food spikes. This is because algae would have less potential impact on the food chain and on any food that could be consumed by humans. In addition, Cereplast also believes that algae help in the process of greening the plastics as well as to ensure for longer term sustainability.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Introduction

This research is being conducted based on the experimental work. In this research species of red algae *Eucheuma cottonii* is used. This algae is being collected from Semporna, Sabah.

During this study, thermo-plastic as well as thermo-mechanical processing will be used to produce plastic. In thermo-plastic processing, the proteins from the red algae are mixed with the plasticizers by using the extruder in order to obtain a homogeneous phase in a dough-like material. Meanwhile thermo-mechanical processing is used further for the application of both heat and pressure. These methods would enable to produce bioplastics which is environmental friendly and to reduce the consumption of petrochemical products.

## 3.2 Materials

### 3.2.1 Denaturants

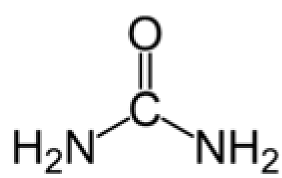
Denaturants basically cause a chemical reaction, whereby protein unfolds when it comes into contact with denaturant chemical.

### 3.2.1.1 Urea

Urea is classified under the group of chaotropes which are one form of denaturants which eventually disrupt water interactions and assist to solubilize hydrophobic proteins and peptides. Moreover it also act as general protein denaturants whereby they unfold proteins and altering their three dimensional structure. Besides that, urea is also known as a low ultraviolet (UV) absorbing protein denaturant.

Urea or carbamide is an organic compound with the chemical formula (NH2)2CO. The molecule has two amine (-NH2) groups which is joined by a carbonyl (C=O) functional group. Properties of urea are stated as below in the table below:

**Table 3.1** Properties of Urea

| | |
|---|---|
| Other names | Carbamide, carbonyl diamide, carbonyldiamine, diaminomethanal, diaminomethanone |
| Molecular Structure |  |
| CAS Number | 57-13-6 |
| Molecular formula | $CH_4N_2O$ |
| Molar mass | 60.06 g mol−1 |
| Appearance | White solid |
| Density | 1.32 g/cm3 |
| Melting point | 133–135 °C |

3.2.1.2 Sodium Dodecyl Sulfate (SDS)

Sodium lauryl sulfate (SLS), sodium laurilsulfate or sodium dodecyl sulfate (SDS or NaDS) ($C_{12}H_{25}SO_4Na$) is an anionic surfactant used in many cleaning and hygiene products. Basically, the molecule has a tail of 12 carbon atoms, attached to a sulfate group, giving the molecule the amphiphilic properties required of a detergent.
Properties of Sodium Dodecyl Sulfate are listed in the table below:

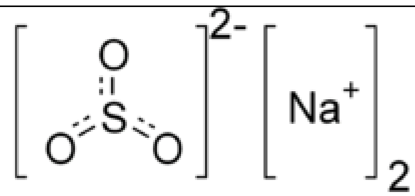
**Table 3.2** Properties of Sodium Dodecyl Sulfate

| | |
|---|---|
| Other names | Sodium monododecyl sulfate; Sodium lauryl sulfate; Sodium monolauryl sulfate; Sodium dodecanesulfate; dodecyl alcohol, hydrogen sulfate, sodium salt; n-dodecyl sulfate sodium; Sulfuric acid monododecyl ester sodium salt; |
| Molecular Structure |  |
| CAS Number | 151-21-3 |
| Molecular formula | $NaC_{12}H_{25}SO_4$ |
| Molar mass | 288.38 g $mol^{-1}$ |
| Density | 1.01 $g/cm^3$ |
| Melting Point | 206 °C |

3.2.1.3 Sodium Sulfite ($Na_2SO_3$ )

Sodium sulfite (sodium sulphite) is a soluble sodium salt of sulfurous acid. A part of the flue gas desulphurization process which produces sodium sulfite resulting from sulfur dioxide scrubbing. Sodium sulfite is primarily used in the pulp and paper industry. It is used in water treatment as an oxygen scavenger agent, in the photographic industry to protect developer solutions from oxidation and (as hypo clear solution) to wash fixer (sodium thiosulfate) from film and photo-paper emulsions, in the textile industry as a bleaching, desulfurizing and chlorinating agent and in the leather trade for the sulfurization of tanning extracts. Properties of sodium sulfite are tabulated as follows:

**Table 3.3** Properties of Sodium Sulfite

| | |
|---|---|
| Other names | Hypo clear (photography) |
| Molecular Structure |  |
| CAS Number | 7757-83-7 |
| Molecular formula | $Na_2SO_3$ |
| Molar mass | 126.043 g/mol |
| Density | 2.633 g/cm3 (anhydrous)<br>1.561 g/cm3 (heptahydrate) |
| Melting Point | 33.4 °C (dehydration of heptahydrate)<br>500°C (anhydrous) |
| Appearance | White Solid |

3.2.1.4 Starch

Starch is being added in order to improve the gluing strength. Starch or amylum is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. This polysaccharide is produced by all green plants as an energy store. It is the most important carbohydrate in the human diet and is contained in such staple foods as potatoes, wheat, maize (corn), rice, and cassava. Properties of starch are listed as follows:

**Table 3.4** Properties of Starch

| | |
|---|---|
| Starch |  |
| CAS Number | 9005-25-8 |
| Molecular formula | $(C_6H_{10}O_5)_n$ |
| Density | 1.5 g/cm3 |
| Melting Point | Decomposed |
| Appearance | White Powder |

**3.2.2 Plasticizers**

Basically, plasticizers are molecules with low molecular weight and low volatility which eventually reduce the intermolecular forces and increase the polymer chains mobility. The less plasticizer, the stronger the plastic but the presence of too much plasticizer would also because plastic becomes too tacky.

3.2.2.1 Glycerol

Glycerol (or glycerin, glycerine) is a simple polyol compound. It is a colourless, odorless, viscous liquid that is widely used in pharmaceutical formulations. Basically, glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. In addition, the glycerol backbone is central to all lipids known as triglycerides. Glycerol form cross links with proteins, the protein